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Electrochemical Redox of PEDOT-Coated Core-Shell Silica Spheres Stabilized in a PEG-Based Hydrogel Maxtrix: Modulation of the Optical Properties by Doping with Various Oxidative Mediators

Jamie. C. Sharp Norton[1]*, Moon G. Han*[2]*, Stephen Creager*[1]*, and Stephen H. Foulger*[2,*]

[1] Department of Chemistry, Clemson University, Clemson, SC. Fax: 864-656-6613; Tel: (864) 656-4995, USA
[2] Center for Optical Materials Science and Engineering Technologies, School of Materials Science and Engineering, Clemson University, Clemson, SC. Fax: (864) 656-1099; Tel: (864) 656-1049, USA
[*]E-mail: foulger@clemson.edu

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In-situ electrochemical methods involving both oxidative and reductive mediators were employed to modify the oxidation state (doping level) of PEDOT polymers in colloidal dispersions of PEDOT-coated silica core-shell particles. The particle dispersions were prepared in water and then encapsulated in an electrolytic PEG-based hydrogel matrix which was then placed in a spectroelectrochemical cell to allow for redox doping. Modifications of the redox states of the PEDOT coating induced by various redox mediators produced changes in the absorbance characteristics of the colloidal dispersion. Three oxidative mediator systems were studied (MV^{2+} / $Ru(bpy)_3^{2+}$, MV^{2+} / Fe $(bpy)_3^{2+}$, and MV^{2+} / K_2IrBr_6). Of the three, the MV^{2+} / K_2IrBr_6 mediator system was the most suitable for oxidizing (doping) the PEDOT without degradation on the time scales studied.

Keywords: core-shell colloids, redox properties, intrinsically conductive polymers

1. INTRODUCTION

Colloidal crystals [1, 2] have been of interest in the development of new photonic devices. Specifically, systems that undergo self-assembly to generate three-dimensional periodic dielectric structures that exhibit a photonic band gap have been examined [3, 4]. One area of importance is the formation of crystalline colloidal arrays, which are formed from colloidal particles dispersed in a liquid media [5, 6]. Stabilization of these colloidal arrays by particle encapsulation in hydrogel networks [3] has furthered the use of these materials in photonic-related applications [7, 8].

To increase the refractive index contrast, colloids with core-shell morphology have been developed [9, 10]. Poly (3,4-ethylenedioxythiophene) (PEDOT) has been used to generate core-shell particles, which in turn have been used to form self-assembled crystalline colloidal arrays [11].

Since the development of poly(3,4-ethylenedioxythiophene) (PEDOT) in the late 1980s by scientists at Bayer A.G. [12], PEDOT has being investigated in many diverse research fields such as basic polymer science [13] material science [14], electrochemistry [15], electronics [16] and optoelectronics [17–19], photovoltaics [20–22], corrosion protection [23], and biosensors [24]. This broad interest in PEDOT and its derivatives stems from properties like high electrical conductivity, intriguing electrical and spectrochemical properties associated with its low band gap, electrochromic properties and good chemical and electrochemical stability, all of which contribute to this polymer's varied applications [14, 25, 26].

Previous studies of PEDOT and other thiophene polymers in potential windows past the potential of electrochemical stability of the polymer have been done. Voltammetric oxidation of PEDOT at potentials up to 3.0V vs.Ag/AgCl yielded a strong double and irreversible oxidation peak [27] and such treatment led to loss of reversible voltammetric signals in the material. Degradation was found to start at 1.9Vvs.Ag/AgCl [28] for PEDOT, and by comparing this value with an onset value of approximately 1.4V vs.Ag/AgCl for oxidative degradation of other polythiophenes [29], it can be seen that PEDOT is indeed an electrochemically stable material, albeit one that can be irreversibly degraded under sufficiently oxidizing conditions.

Previous work from our laboratory [30, 31] demonstrated electrochemical modulation of the optical properties of PEDOT-on-silica core-shell particle suspensions and crystalline colloidal arrays in a stabilizing polyether hydrogel matrix using redox mediators that were electrogenerated *in-situ*. The changes in absorbance of these films at 800 nm are correlated with electrochemical de-doping and re-doping of PEDOT-containing particles in spatially isolated regions. The doping (oxidation) process utilized electrochemically generated elemental bromine (Br_2, an oxidant with E^o = +888 mV vs. Ag/AgCl) as the oxidizing agent to dope the PEDOT polymer by using a combination of tris(2,2'-bipyridyl) ruthenium (II) chloride ($Ru(bpy)_3^{2+}$, E^o = 1050 mV vs. Ag/AgCl) [20] as oxidizing agent (in the Ru(III) form) and potassium bromide as precursor to produce Br_2 which ultimately dopes the polymer. The de-doping (reduction) process used dimethyl viologen dichloride, MV^{2+}, E^o = -645 mV vs. Ag/AgCl as the reducing agent. In the prior work [30], absorbance corresponding to re-doped PEDOT never fully recovers to its initial value following electrochemical de-doping and re-doping when using bromineand $Ru(bpy)_3^{3+}$ to accomplish doping, and after extended electro-oxidative treatment, a complete bleaching of the PEDOT absorbance was observed. This chemical bleaching could possibly be prevented by using different, perhaps less potent mediators. Tris(2,2'-bipyridyl) ruthenium (II) chloride ($Ru(bpy)_3^{3+}$) alone

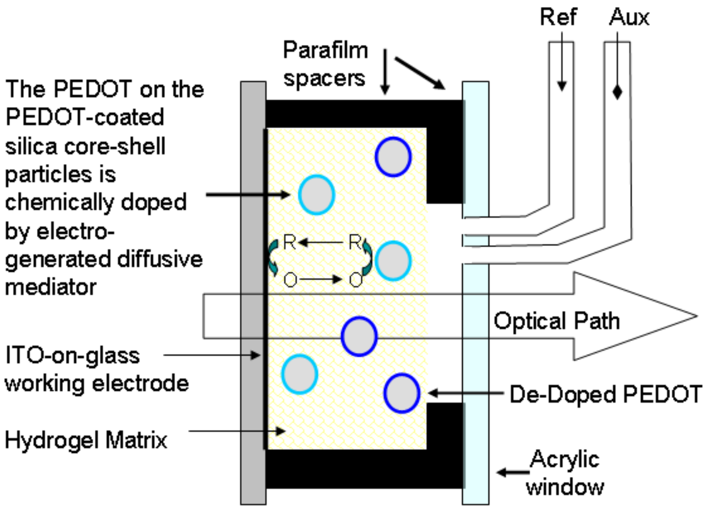

Figure 1. A schematic diagram of the spectro-electrochemical cell used in this work to monitor the electrochemical doping / de-doping of hydrogel-stabilized PEDOT-containing films. Films are placed atop ITO-coated-glass working electrodes which are then fitted with spacers and acrylic window containing entry ports for the reference and auxiliary electrodes. The entire assembly was sealed with epoxy prior to use. An enlarged view illustrates the mediated electrochemical doping / de-doping of PEDOT in the core-shell PEDOT-coated silica particles.

is a powerful electrochemical catalyst for oxidation, and without the addition of bromide may itself prove to be a suitable dopant for PEDOT since bromination of the PEDOT double bonds is a potential degradation pathway for the polymer. A second, less oxidizing mediator, tris(2,2'-bipyridyl) iron (II) chloride ($Fe(bpy)_3^{3+}$, E^o = 871 mV vs. Ag/AgCl), was also selected for study since its $E^{o\prime}$ is about 180 mV less positive than that of $Ru(bpy)_3^{3+}$. A third oxidative mediator, potassium hexabromoiridate (K_2IrBr_6), E^o = 606 mV vs. Ag/AgCl [32,33] was also investigated since its E^o is about 270 mV less positive than either bromine or $Fe(bpy)_3^{3+}$ and 450 mV less positive than $Ru(bpy)_3^{3+}$. Also, this redox mediator is negatively charged, unlike the metal polypyridyl complexes which are all positively charged. Various iridium complexes have been used as electrochemical catalysts for oxidation. One study examined the feasibility of insulin detection based on the oxidation of insulin by aquated chloro complexes of iridium (IV) [34]. Another study investigated the development of iridium (IV) compounds such as IrO_2 into films as the catalyst for water oxidation [35]. The iridium (IV) halogen complexes are soluble in aqueous solutions and are easily reduced to Ir (III) state. The Ir (IV)/ Ir (III) hexabromide system was selected for this work, because it is a milder oxidant than $IrCl_6^{2-}$/ $IrCl_6^{3-}$ system, E^o = 668 mV vs. Ag/AgCl [34].

The scope of this work involves the selection of alternative mediators with different oxidizing strengths that are able to dope the PEDOT without also irreversibly oxidizing (bleaching) it. Switching the oxidation states of PEDOT-coated core-shell silica particles (150 nm diameter) was accomplished in hydrogel-stabilized aqueous electrolyte solutions using the following electrogenerated oxidizing agents: tris(2,2'-bipyridyl) ruthenium (II) chloride ($Ru(bpy)_3^{3+}$, E^o = 1050 mV vs. Ag/AgCl; tris(2,2'-bipyridyl) iron (II) chloride ($Fe(bpy)_3^{3+}$, E^o =

871 mV vs. Ag/AgCl); and potassium hexabromoiridate (K_2IrBr_6), E° = 606 mV vs. Ag/AgCl. In general the more strongly oxidizing mediators were found to be capable of doping the PEDOT particles but with associated oxidative degradation. The weaker oxidants were less effective, but also less prone to induce oxidative degradation. The negatively-charged iridium mediator was especially effective; it produced almost complete oxidative doping with an absence of oxidative degradation over a timesacle of many tens of hours.

2. RESULTS AND DISCUSSION

The cell used to acquire both electrochemical and spectroscopic data consisted of an indium-doped tin oxide (ITO)-coated glass working electrode, a platinum wire auxiliary electrode, and a silver wire quasi-reference electrode. Two parafilm spacers, each 250 μm thick, were stacked in the cell to give an overall cell thickness of 500 μm. The first spacer holds the PEDOT film against the ITO electrode and defines the active region of the electrode surface as an 18 mm diameter circle. The second spacer has a slightly smaller diameter of 17 mm, such that the PEDOT-containing hydrogel film (produced as described in the experimental section) is held securely against the ITO electrode surface. An acrylic top is firmly placed on top of the spacer stack to create the thin-layer cavity, and the entire cell is sealed with epoxy prior to use. Figure 1 illustrates this cell design.

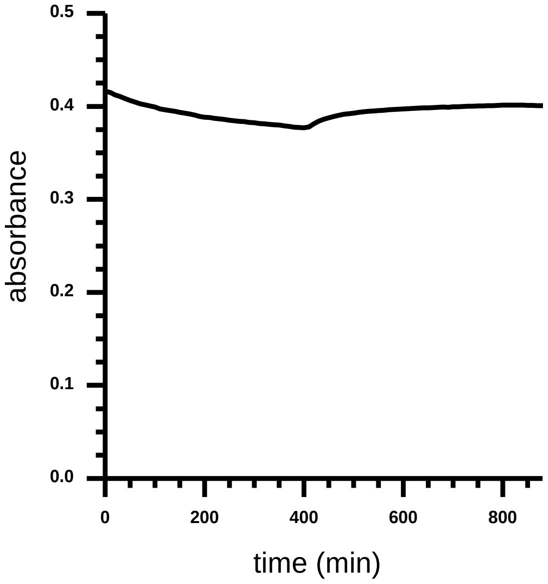

Figure 2. Absorbance change at 800 nm for a hydrogel-stabilized film of PEDOT-coated silica particles in the spectro-electrochemical cell shown in Figure 1with no redox mediators present. The film was subjected to a potential program with a reducing potential (–775 mV vs. Ag wire) for 400 min, followed by application of an oxidizing potential (+1275 mV vs. Ag wire) for 400 min.

The total cell volume, not including the inlet tubes for the reference and auxiliary electrodes, is approximately 120 μL. In a typical experiment, the cell was filled with a buffer solution consisting of 25mM KCl, 25 mM $KClO_4$, and50 mM phosphate atpH 7.2. In some cases, redox mediators and/or potassium bromide were also present in the buffer solution. When redox mediators were present, their concentrations were as follows: 0.1mM of reductive mediator (dimethyl viologen dichloride, MV^{2+}), and 0.1 mM of oxidative mediators (tris(2,2'-bipyridine)ruthenium (II) chloride, $Ru(bpy)_3^{2+}$, tris(2,2'-bipyridine)iron (II) perchlorate, $Fe(bpy)_3^{2+}$ and potassium hexabromoiridate, K_2IrBr_6). When bromide was present in the buffer solution, it was added as 25 mM KBr for the $Ru(bpy)_3^{2+}$ and $Fe(bpy)_3^{2+}$ systems and 100 mM KBr for the K_2IrBr_6 system. Hydrogel-stabilized films containing PEDOT-coated silica particles on ITO glass were prepared for spectro-electrochemical experiments by gently shaking them in the various redox mediator-containing buffer solutions on a Vari-mix shaker for twelve hours. The films were then placed in fresh mediator solutions that were nitrogen-purged to remove ambient oxygen, then sealed inside the electrochemical cell using epoxy.

A key aim of this work is to investigate the spectral changes that are obtained when using electrogenerated redox mediators of varying oxidative strength in suspensions of isolated PEDOT-containing particles that are dimensionally stabilized in a polyether hydrogel matrix. For the de-doping (reduction) process, methyl viologen (MV^{2+}, E^o = -645 mV vs. Ag/AgCl) [19] was still used as the reductive mediator since it was shown in previous work [30, 31] to be a strong enough reducing agent to accomplish PEDOT de-doping.

For monitoring the dynamics of electrochemical doping / de-doping / re-doping of PEDOT in these films, it is useful to construct plots of absorbance vs. time at a wavelength 800 nm, during application of a potential program to the ITO electrode, which accomplishes sequential PEDOT de-doping and re-doping.

The absorbance vs. time at 800 nm was selected since at this wavelength the doped PEDOT absorbs strongly but the de-doped PEDOT absorbs hardly at all. Control spectroelectrochemical experiments showed low absorbance at this wavelength for solutions containing only the redox mediator cocktail of MV^{2+} with either $Ru(bpy)_3^{2+}$, $Fe(bpy)_3^{2+}$ or $IrBr_6^{3-}$ each at 0.1 mM, and no PEDOT, over the full range of potentials applied in this work.

Figure 2 presents an absorbance plot at 800 nm vs. time for hydrogel-stabilized PEDOT-silica core-shell particle films soaked with a solution that contained buffer and electrolyte, including some potassium bromide but no mediator. This film shows some small absorbance changes that correlate with the periodic application of reducing and oxidizing potentials to the ITO electrode.

The absorbance changes that were observed in the absence of mediators (Figure 2) are believed to be caused by direct PEDOT oxidation / reduction in a small population of PEDOT-silica particles that may have settled onto the ITO electrode surface during the hydrogel curing step, and/or that may have formed a percolating particle network in which direct electrooxidation / reduction could occur within the network of contacting particles.

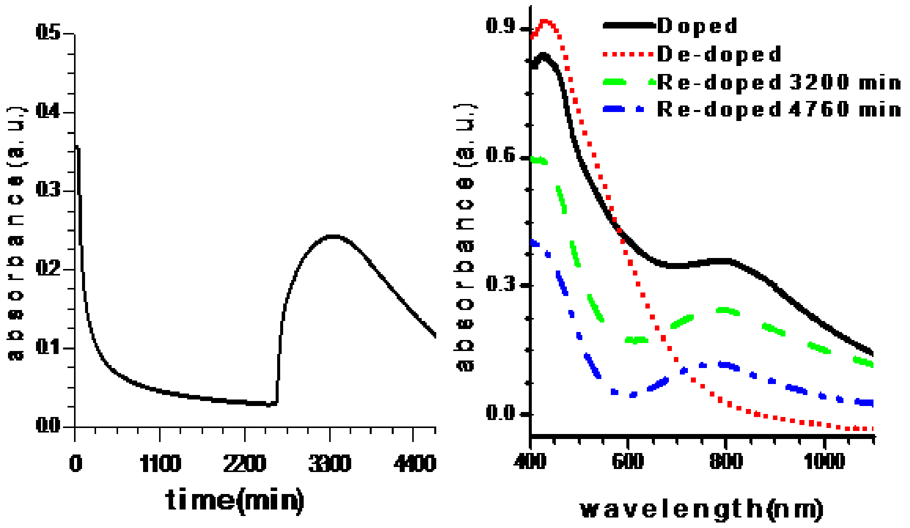

Figure 3. Absorbance change at 800 nm (left) and from 400 nm to 1100 nm (right) for a hydrogel-stabilized film of PEDOT-coated silica particles in the spectro-electrochemical cell show in Figure 1. The cell was filled with a 50 mM phosphate buffer at pH 7.2 containing 25mM KCl, and 25 mM $KClO_4$ and the MV^{2+} / $Ru(bpy)_3^{2+}$redox mediators.

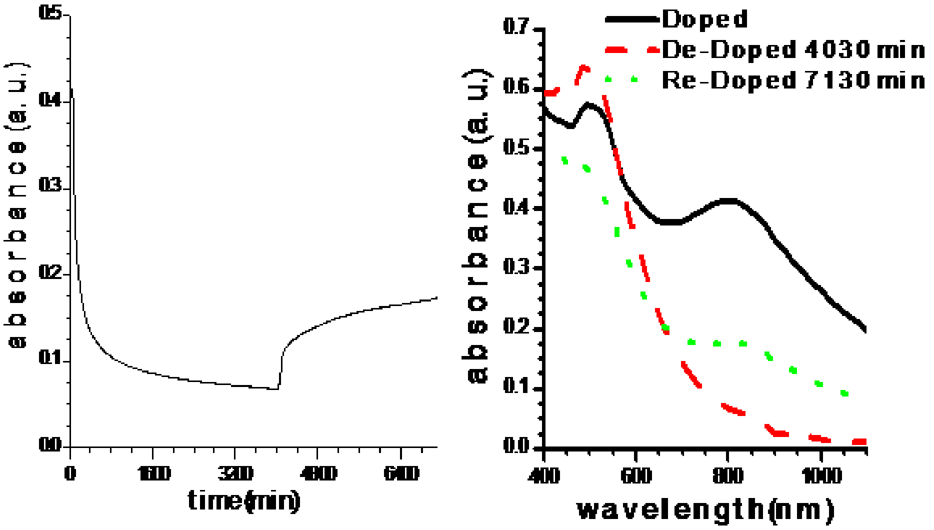

Figure 4. Absorbance change at 800 nm (left) and from 400 nm to 1100 nm (right) for a hydrogel-stabilized film of PEDOT-coated silica particles in the spectro-electrochemical cell shown in Figure 2.1. The cell was filled with a 50 mM phosphate buffer at pH 7.2 containing 25mM KCl, 25 mM $KClO_4$, and the MV^{2+} / $Fe(bpy)_3^{2+}$redox mediators. The film underwent a reductive potential step at –775 mv for 4040 minutes (67.3 hours) followed by an oxidative potential step at 1100 mV for 3090 minutes (51.5 hours).

Figure 3 presents another data set of absorbance vs. time for the MV^{2+} / $Ru(bpy)_3^{2+}$ mediator system without KBr, which more thoroughly considers the use of $Ru(bpy)_3^{2+}$ as the oxidative mediator. The cell contained a hydrogel-stabilized film of PEDOT-coated silica particles with the MV^{2+} / $Ru(bpy)_3^{2+}$ redox mediators present, as well as buffer and electrolyte, but did not contain potassium bromide. The film underwent a reductive potential step at –775 mv for 2670 min (44.5 hours) followed by an oxidative potential step at 1275 mV for 2090 minutes (24.8 hours).The absorbance vs. time trace of the film in the MV^{2+} / $Ru(bpy)_3^{2+}$ redox mediator system illustrates an effect very similar to the one seen of this mediator system in the presence of KBr from previous work [30]. The absorbance corresponding to re-doped PEDOT never fully recovers to its initial value following electrochemical de-doping. The absorbance corresponding to re-doping peaks at approximately 3200 min, 820 minutes after the application of the oxidizing potential, and then begins to gradually decrease, eventually reaching a much reduced value after 2160 minutes at the oxidizing potential. Apparently the electrogenerated $Ru(bpy)_3^{3+}$ even in the absence of KBr can dope the PEDOT on a timescale of hundreds of minutes but on a somewhat longer timescale it can irreversibly oxidize the polymer as indicated by the loss of light absorbance for the film (Figure 3, right).

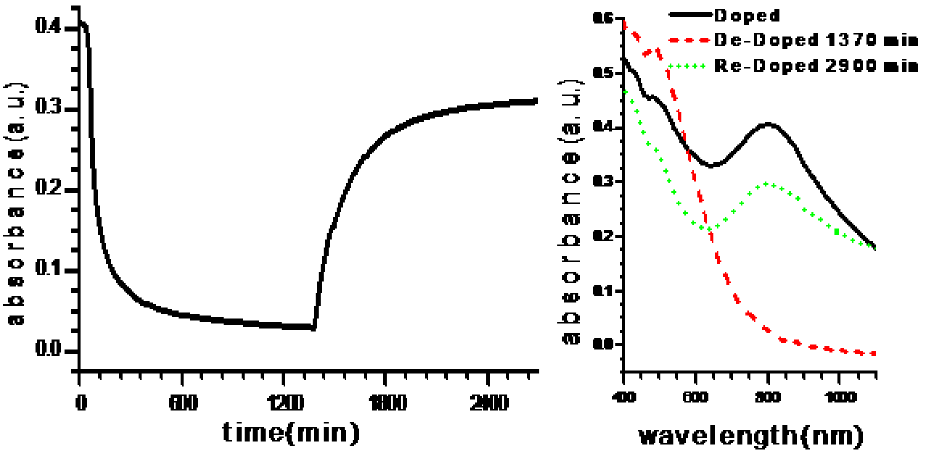

Figure 5. Absorbance change at 800 nm (left) and from 400 nm to 1100 nm (right) for a hydrogel-stabilized film of PEDOT-coated silica particles in the spectro-electrochemical cell shown in Figure 1. The cell was filled with a 50 mM phosphate buffer at pH 7.2 containing 25mM KCl, 25 mM $KClO_4$, and the MV^{2+} / $Fe(bpy)_3^{2+}$redox mediators. The film underwent a reductive potential step at –775 mv for 4040 minutes (67.3 hours) followed by an oxidative potential step at 1100 mV for 3090 minutes (51.5 hours).

The observation of PEDOT bleaching by $Ru(bpy)_3^{3+}$ led to the selection of the $Fe(bpy)_3^{2+}/Fe(bpy)_3^{3+}$ system as a milder oxidative mediator with a redox potential about 180 mV less positive than that of the $Ru(bpy)_3^{2+}$ / $Ru(bpy)_3^{3+}$ system. Figure 4 (left) presents absorbance at 800 nm vs. time plots for a hydrogel-stabilized PEDOT-silica core-shell particle film, each of which was subjected to cycles of a potential program involving initial application of a reducing potential (–775 mV vs. Ag wire), followed by application of an oxidizing potential (+1100 mV vs.

Ag wire). The film shows a rapid decrease in absorbance at 800 nm that correlates with application of the reducing potential to the ITO electrode. However, the absorbance changes for the PEDOT re-doping with $Fe(bpy)_3^{3+}$ are modest and slow. In fact, absorbance changes for oxidative doping with $Fe(bpy)_3^{3+}$ are not much larger than those seen with no mediators at all (Figure 2). The absorbance corresponding to re-doping of PEDOT never recovers to its initial value following electrochemical de-doping (Figure 4, right), and the level of re-doping is much lower when compared to the MV^{2+} / $Ru(bpy)_3^{2+}$ redox mediator system (Figure 4.2).

Figure 5 (left) presents the absorbance at 800 nm vs. time for a hydrogel-stabilized PEDOT-silica core-shell particle film with the MV^{2+} / K_2IrBr_6 redox mediator system. The potential program involved an initial application of a reducing potential (–775 mV vs. Ag wire), followed by application of an oxidizing potential (+600 mV vs. Ag wire). The film shows absorbance changes that correlate with the periodic application of reducing and oxidizing potentials to the ITO electrode. The absorbance corresponding to re-doped PEDOT recovers nearly to its initial value following electrochemical de-doping and re-doping and is similar in magnitude when compared to the MV^{2+} / $Ru(bpy)_3^{2+}$ redox mediator system (Figure 3). Significantly, the absorbance following re-doping does not appear to decline on this time scale, unlike for the MV^{2+} / $Ru(bpy)_3^{2+}$ redox mediator system. This indicates that the $IrBr_6^{2-}$/ $IrBr_6^{3-}$ system can dope the PEDOT without irreversibly oxidizing the polymer as indicated by no loss of light absorbance for the film (Figure 5, right). The ability of $IrBr_6^{2-}$/ $IrBr_6^{3-}$ to act as a better dopant than $Fe(bpy)_3^{2+}$/$Fe(bpy)_3^{3+}$, even though the redox potential of the iridium complex is over 250 mV less positive than the iron complex, may stem from the negative charge of the $IrBr_6^{3-}$ vs. the positive charge of the $Fe(bpy)_3^{3+}$. As PEDOT is doped, it develops a positive charge that could electrostatically repel the $Fe(bpy)_3^{3+}$ trication. This repulsion could account for the limited oxidation seen with the $Fe(bpy)_3^{3+}$ mediator. The $IrBr_6^{3-}$ is negatively charged and would not be repelled, as the PEDOT coating the silica particles is doped and adopts a more positive charge. The use of a negatively-charged dopant could facilitate doping because the dopant could more easily access regions of polymer by ion exchange that might not be accessible to dopants that cannot undergo ion exchange. This finding is significant because is lends insight into how best to choose a redox mediator / dopant to achieve complete doping of a PEDOT-based material, on as rapid a timescale as possible, with a minimum of prospects for irreversible oxidative degradation.

3. CONCLUSIONS

This work demonstrates electrochemical modulation of the optical properties of PEDOT-on-silica core-shell particle suspensions in a stabilizing polyether hydrogel matrix using electrogenerated oxidizing and reducing agents. Changes in absorbance at 800 nm are correlated with electrochemical de-doping and re-doping of PEDOT-containing particles in spatially isolated regions by electrogenerated redox mediators that diffuse between the ITO electrode where they are generated and the isolated PEDOT-containing particles throughout the hydrogel film. Of the mediator systems studied (MV^{2+} / $Ru(bpy)_3^{2+}$, MV^{2+} / Fe $(bpy)_3^{2+}$, and MV^{2+} / K_2IrBr_6), the MV^{2+} /

K_2IrBr_6 mediator system was the most suitable for oxidizing the PEDOT without degrading it on the time scales studied.

Notes and references

‡ Experimental

Synthesis of Potassium Hexabromoiridate (IV)

The preparation of potassium hexabromoiridate (K_2IrBr_6) has been described elsewhere (33). In brief, 0.25 g of ammonium hexachloroiridate (IV) and 0.81 g of potassium bromide was dissolved in 25 mL of deionized water. The solution was purged with nitrogen gas for 20 minutes followed by heating for 48 hours. The solution volume was reduced to approximately 5 mL by evaporation, then 50 mL of 48% hydrobromic acid was added to cause precipitation of KCl and KBr crystals, which were then removed by filtration. The filtrate was then evaporated to approximately 5 mL, cooled to room temperature, and then 0.2 mL of bromine was added and the mixture was returned to a boil to remove excess bromine. Once cooled, purple crystals of potassium hexabromoiridate precipitated from the solution. The crystals were filtered and washed with 5% KBr and ethanol and were allowed to air dry with a yield of about 0.18 g (72%) of potassium hexabromoiridate (K_2IrBr_6).

Preparation of poly(3,4-ethylenedioxythiophene)
(PEDOT)-coated silica particles and hydrogel stabilized films

The synthesis of PEDOT-coated silica particles has been described in detail elsewhere (11). A brief description follows. Commercially available silica particles in an aqueous suspension were centrifuged at 8,000 rpm for 30 mins to remove smaller particles. The larger particles were collected from the bottom of the centrifuge tubes and then re-dispersed in deionized water by sonication, leading to a suspension for which the average particle diameter was 135 nm (as measured by dynamic light scattering, DLS).

A 6 g (solid weight) quantity of silica sol with the smaller particles removed as described above was dispersed in 140 mL of deionized water, and to this solution was added 0.436 g of EDOT dissolved in 40 mL of methanol. The mixture was stirred for 2 hours. Polymerization was initiated by adding 1.81 g of APS oxidant dissolved in 20 mL of deionized water. The reaction was allowed to proceed at 30 ^{o}C for 18 hours. Polymerization was terminated by adding methanol to the reaction mixture, and the resulting particles were purified by repetitive centrifugation and re-dispersion with water and methanol to produce a suspension of PEDOT-coated silica particles with an average particle diameter of 147 nm (as measured by DLS) and a PEDOT coating of 6 nm. This particle suspension exhibits opalescence after several cycles of the cleaning processes. A second batch of PEDOT-coated silica particles was made using the method above, which began with silica particles 151 nm in diameter, which produced coated particles with a diameter of 164 nm, yielding a PEDOT coat of about 7 nm.

The preparation of hydrogel-stabilized films containing PEDOT-coated silica particles has also been described elsewhere [6]. In brief, the hydrogel matrix used to stabilize the colloidal PEDOT-silica particle suspensions was generated from an aqueous solution consisting of PEG-MA monomer, PEG-DMA crosslinker, DEAP photoinitiator, and a particle suspension in water, in a mass ratio of 100.10:1.5:500. The latter mass corresponds to a solution that contained 23% by weight PEDOT-coated silica particles dispersed in deionized water. For the pure silica particle hydrogel films, an aqueous dispersion of 23% by weight silica particles was used in place of the dispersion of PEDOT-on-silica particles. In each case, the mixture was placed into a glass cell consisting of two treated glass slides and a 250 μm thick parafilm spacer with an 18 mm diameter hole cut in the center. The glass slide surfaces were made hydrophobic prior to use by coating them with a 30% octadecyl trichlorosilane (OTS) in toluene solution after cleaning with piranha reagent. Polymerization was initiated by exposure of the mixture to UV light from a Kepro UV exposure frame model BTX-200A for 8 minutes on each side.

Spectro-electrochemical cell and measurements

A CH Instruments model 660B electrochemical workstation was used for acquiring cyclic voltammograms and for applying the requisite potential programs while the optical absorption data were simultaneously acquired on a Perkin Elmer Lambda 900 UV-vis absorption spectrophotometer. The spectrometer was set to automatically acquire an absorption spectrum every 10 minutes at a scan speed of 150 nm per minute, scanning from 400 nm to 1100 nm. A hydrogel-stabilized film containing only silica particles, with no PEDOT, with the same particle concentration as for the films containing PEDOT-coated silica particles was used as the spectral reference.

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